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(54) Title: METHOD FOR FRACTIONATION OF SUCROSE-CONTAINING SOLUTIONS

(57) Abstract

The invention relates to a method for separating sucrose and a second dissolved component from a beet-derived sucrose-containing solution, wherein the solution is subjected to a first fractionation by a chromatographic simulated moving bed method to yield a sucrose-enriched fraction and a fraction ennched with the second dissolved component, or a fraction enriched with sucrose and the second component, and the resulting fraction enriched with the second component or with sucrose and the second component is subjected to a second chromatographic fractionation, to yield a second sucrose-enriched fraction and a separate fraction enriched with the second dissolved component.

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Method for fractionation of sucrose-containing solutions

The present invention relates to a method for separating sucrose and additionally a second dissolved component from a solution. More particularly, the invention relates to a method in which a solution containing sucrose and other dissolved substances is first fractionated by a chromatographic simulated moving bed (SMB) method to yield a sucrose-enriched fraction and a fraction enriched with a second component to be recovered, or a fraction enriched with sucrose and said second component, and the fraction enriched with said second component and optionally sucrose is further fractionated chromatographically, either by a batch method or a simulated moving bed method. In a preferred embodiment, the invention relates to the fractionation of a beet-derived sucrose-containing solution to yield a sucrose-enriched fraction and a fraction enriched with a second organic compound commonly present in beet-derived solutions, such as betaine, inositol, raffinose, galactinol, or serine and other amino acids.

The description hereinbelow employs the established abbreviation SMB for the simulated moving bed, which is customary in the art of chromatography.

It is known that sucrose and betaine are recoverable from molasses by chromatographic separation methods. International published application WO 81/02420, which corresponds to Finnish Patent 77,845 to Suomen Sokeri Oy, describes a chromatographic method for the recovery of betaine from molasses by a batch process in which diluted molasses is fractionated with a polystyrene sulphonate cation exchange resin in alkali metal form. This method achieves good separation of sucrose and betaine. This reference also discloses a method in which a betaine-enriched fraction obtained from a first

fractionation is subjected to further chromatographic purification. The further purification step is capable of separating the other components of the betaine-enriched fraction. However, the dry solids content in the sucrose and betaine fractions obtained by this method is relatively low, therefore, large amounts of eluant water must be evaporated in recovering the sucrose and betaine from the respective fractions by crystallization.

Continuously operated chromatographic separation processes nowadays commonly employ the SMB method, which method is used in a variety of different applications. The SMB method has a separating performance that is several times higher than that of the batch method, and also results in significantly lower dilution of the products or, conversely, lower consumption of eluant.

The SMB method may be carried out in either a continuous or a sequential mode. In a continuous SMB method, which was first disclosed in the early 1960s in U.S. Patent 2,985,589, all fluid streams typically flow continuously. These streams are: supply of feed solution and eluant, recycling of liquid mixture, and withdrawal of products. The flow rate for these flows may be adjusted in accordance with the separation goals, i.e. increased yield, purity, or capacity. Separation of sucrose by such continuous SMB methods has been described in international published application WO 91/08815 by The Amalgamated Sugar Company and in U.S. Patent 4,990,259 to M. M. Kearney and M.W. Mumm and assigned to The Amalgamated Sugar Company.

In a sequential SMB method, the pattern of fluid streams is the same as in the continuous SMB method, but some of the fluid streams do not flow continuously. Sequential SMB fractionation methods in which a sucrose fraction and a betaine fraction are recovered from beet

molasses are disclosed in Finnish Patent 86,416 to Suomen Sokeri Oy, which corresponds to U.S. Patent 5,127,957, and international published application WO 94/17213 to Suomen Sokeri Oy. German Offenlegungsschrift 4,041,414 to Japan Organo Co, which corresponds to British published application 2,240,053, also discloses a sequential SMB method by which several product fractions are recovered from sugarbeet molasses.

In the sugar industry, the important parameters in the fractionation of molasses to recover sucrose include the purity and yield of sucrose, the separation capacity, and the eluant/feed ratio. A purity of 92% and a yield of 90% are the usual requirements for a sugar product. In order to increase the capacity, the flow rates, which are generally higher in SMB processes than in batch processes, are increased. Along with the increase in the flow rate, however, a "flat tail" is produced in the sucrose elution profile. This is especially disadvantageous when it is desired to recover, in addition to sucrose, a second dissolved component. With respect of the recovery of sucrose and betaine, this effect is apparent upon comparison of the elution profiles presented in international application WO 81/02420 and Finnish Patent 86,416, for example. In the course of obtaining a high sucrose yield, the betaine yield is diminished because part of the betaine is allowed to pass into the sucrose fraction wherefrom it is removed in the sucrose crystallization step. Likewise, if a high betaine yield is desired, considerable amounts of sucrose end up in the betaine fraction, thus diminishing the sucrose yield and considerably impairing the purity of the betaine fraction.

In the above references, the purity of the betaine fraction obtained by the process of German Offenlegungsschrift 4,041,414 is relatively good, 80.9% on a

dry solids basis (d.s.), but the purity of the sucrose fraction, 87% d.s., is inadequate in view of the needs of the sugar industry. It can be concluded from the composition of the feed solution of Example 3 in said reference that the "thin juice" was demineralized prior to the SMB fractionation by the "KAAK method" (which refers to cation exchange - anion exchange - anion exchange - cation exchange as described in Sayama, K., Kamada, T., and Oikawa, S., *Production of Raffinose: A New By-Product of the Beet Sugar Industry*, British Sugar plc, Technical Conference, Eastbourne 1992). Molasses produced by such a beet sugar process has a different composition from common molasses. Typically, beet molasses contains 1.5-3.5% by weight of raffinose and 3.5-6.5% of betaine on a dry solids basis. On the other hand, since the feed solution of Example 3 in German Offenlegungsschrift 4,041,414 has a raffinose content of 17.3% by weight and a betaine content of 12.2% by weight dry solids basis, it can be concluded, on the basis of the raffinose-to-betaine ratio, that roughly half of the betaine contained in common beet molasses was lost (obviously in the ion exchange treatment).

In accordance with the results presented in Finnish Patent 86,416, a purity as high as 70.9% d.s. for the betaine fraction was obtained (11.1% d.s. of sucrose present). However, the 86.8% purity of the sucrose fraction does not meet the requirements of the sugar industry. Similarly, the 47.5% purity of the betaine fraction reported in international application WO 94/17213 is rather poor.

The object of the present invention is a fractionation method by which sucrose and additionally a second desired organic component, such as betaine, inositol, raffinose, galactinol, or serine and other amino acids, can be recovered from a beet-derived sucrose-containing

solution so as to obtain higher yields and at least equivalent purity for sucrose.

It is another object of the present invention to fractionate sucrose and betaine so as to obtain higher yields and/or higher purity for the second recovered component, specifically betaine, as compared with the results obtained by the prior SMB methods.

It is a further object of the invention to provide an economical fractionation in terms of capacity and the eluant/feed ratio - at least equivalent to the prior SMB methods for fractionating sucrose-containing solutions.

These objects are achieved with the method of the invention for separating sucrose and additionally a second dissolved component from a sucrose-containing solution, in which method the solution is subjected to a first chromatographic fractionation by a SMB method to yield a sucrose-enriched fraction (hereinafter the first sucrose fraction) and a fraction enriched with the second dissolved component, and the resulting fraction enriched with the second component is subjected to a second chromatographic fractionation, to yield a second sucrose-enriched fraction (hereinafter the second sucrose fraction) and a separate fraction enriched with the second dissolved component.

The first fractionation may be carried out in such a way that sucrose and the second component are enriched in the same fraction.

In accordance with a preferred embodiment of the invention, sucrose and said second component are enriched in separate fractions in the first chromatographic fractionation, and the sucrose fraction obtained in the second fractionation is combined with the sucrose fraction from the first fractionation, and sucrose is recovered from the combined sucrose fraction thus

obtained.

In accordance with another preferred embodiment of the invention, sucrose and said second component are enriched in separate fractions in the first chromatographic fractionation, and the second sucrose fraction is returned to the feed solution for the first fractionation. In this embodiment, sucrose is recovered from the first sucrose fraction.

In accordance with another preferred embodiment of the invention, a fraction enriched with sucrose and the second dissolved component is recovered in the first fractionation, and sucrose is recovered from the second sucrose fraction and the second component from the fraction enriched with said second dissolved component obtained from the second fractionation. In this embodiment, the sucrose fraction obtained is pure enough to enable recovery of sucrose by methods commonly used in the sugar industry. The fraction enriched with the second dissolved component obtained from the second fractionation can also be pure enough to enable recovery of said component, e.g. betaine, by conventional techniques.

Generally, the second dissolved component is recovered from the fraction obtained from the second fractionation, which is enriched with the second dissolved component. Part of the second dissolved component can be recovered from a fraction enriched with said second dissolved component obtained from the first chromatographic fractionation. Alternatively, said fraction enriched with said second component obtained from the first chromatographic fractionation is combined with the fraction obtained in said second fractionation, which is enriched with the second dissolved component. The term "second dissolved component" refers to organic compounds commonly present in beet-derived solutions, such as beta-

ine, inositol, raffinose, galactinol, or serine and other amino acids. The second chromatographic fractionation, i.e. fractionation of the fraction enriched with the second dissolved component which is obtained from the first fractionation, may be performed by either a batch method or a SMB method.

The invention is particularly suitable for the recovery of sucrose and betaine from beet molasses. Therefore, the following description of the invention specifically refers to the recovery of sucrose and betaine, but the invention is not so limited. Instead of, or in addition to betaine, any other dissolved organic substance may be similarly recovered by adjusting the process conditions and parameters to suit the separation in question, which can be achieved easily by those skilled in the art.

With the method of the invention, the sucrose yield can be improved by up to about 10 per cent compared with the SMB methods presently employed in the sugar industry. This improvement represents remarkable economic advantages in view of the large amounts of molasses used by the sugar industry for chromatographic separation. For example, in the United States, about 500,000 tonnes d.s. of molasses are currently used per annum.

The purity of the sucrose fraction produced by the method of the invention is consistent with the goal of about 92% set for industrially practised SMB methods.

With regard to betaine, the method of the invention can achieve yields as high as about 95%, as contrasted with prior yields of about 30-70%, and a purity as high as about 95%, as contrasted with purities of about 25-70% (calculated on a dry solids basis) hitherto obtained.

The first chromatographic separation in the

method of the invention may be carried out with prior art SMB methods and apparatus known to be suitable for the fractionation of molasses, such as those disclosed in U.S. Patent 4,402,832 (continuous SMB method), Finnish Patent 86,416, and international application WO 94/17213 (discussed above).

Also the further fractionation of the betaine fraction produced in the first fractionation to yield a second sucrose fraction and a second betaine fraction may be carried out by known chromatographic separation methods and apparatus, for example employing methods and apparatus disclosed in the context of the batch method in international application WO 81/02420 and in the context of SMB methods in Finnish Patent 86,416 and international application WO 94/17213.

In the continuous SMB method, all flows (supply of feed solution and eluant, recycling of liquid mixture, and withdrawal of product fractions) are typically continuous. The rates for these flows may be adjusted in accordance with the separation goals (yield, purity, capacity). There are normally 8 to 20 sectional packing material beds that are combined into a single loop. The feed and product withdrawal points are shifted cyclically in the downstream direction in the packing material bed. On account of the supply of eluant and feed solution, the withdrawal of products, and the flow through the packing material bed, a dry solids profile is formed in the packing material bed. Constituents having a lower migration rate in the packing bed are concentrated in the back slope of the dry solids profile, while ingredients having a higher migration rate are concentrated in the front slope. The points of introduction of the feed solution and eluant and the withdrawal points of the product or products are shifted gradually at substantially the same rate at which the

dry solids profile moves in the packing material bed. The product or products are withdrawn substantially from the front and back slopes of the dry solids profile. The feed solution is introduced substantially at the point where the composition of the cyclically moving dry solids profile is closest to the composition of the feed solution, and the eluant is introduced approximately at the point of minimum concentration of the dry solids profile. Part of the separated products are recycled on account of the continuous cyclic flow, and only part of the dry solids profile is withdrawn from the packing material bed during one sequence.

The feed and withdrawal points are shifted cyclically by using feed and product valves located along the packing material bed, typically at the upstream and downstream end of each sectional packing material bed. If it is desired to recover product fractions of very high purity, short phase times and multiple sectional packing material beds must be employed. The requisite valves and feed and withdrawal equipment are part of the apparatus.

In the sequential SMB system, not all flows (supply of feed solution and eluant, recycling of liquid mixture, and withdrawal of products) are continuous. Yet the shifting of the dry solids profile or profiles moving cyclically in the system is continuous. The flow rate and the volumes of the different feeds and product fractions may be adjusted in accordance with the separation goals (yield, purity, capacity).

During the feeding phase, a feed solution, and possibly also an eluant during a simultaneous eluting phase, is introduced into predetermined sectional packing material beds, and, simultaneously, one or more product fractions are withdrawn. During the eluting phase, eluant is introduced into a predetermined sec-

tional packing material bed or predetermined sectional packing material beds and, during the feeding and eluting phases, one or more product fractions are withdrawn.

During the recycling phase, essentially no feed solution or eluant is supplied to the sectional packing material beds and essentially no products are withdrawn. A forward flow is maintained in a fixed direction in a system comprising at least two sectional packing material beds, and the products are recovered during a multistep sequence comprising the above phases. A sectional packing material bed may comprise one column, or it is possible to pack several successive sectional packing material beds into a single column.

During the feeding phase, feed solution is introduced into a sectional packing material bed and a corresponding quantity of any product fraction is withdrawn at a point which may be located either in the same sectional packing material bed as the feed point (in which case the other sectional packing material beds in the system may be, for example, in the eluting or recycling phase) or in a different sectional packing material bed from that of the feed point, which bed is connected in series (possibly through other sectional packing material beds) with the sectional packing material bed into which the feed is introduced. During the recycling phase, the liquid in the sectional packing material beds, along with its dry solids profile or profiles, is recycled in a loop comprising one, two or several sectional packing material beds. In the eluting phase, eluant is introduced into the packing material bed and a corresponding amount of product fraction(s) is (are) withdrawn from the same or a downstream sectional packing material bed.

As stated previously, a detailed description of

these sequential SMB methods applied to the recovery of sucrose and betaine from beet molasses is provided in Finnish Patent 86,416 and international application WO 94/17213; these processes may be employed in the method of the present invention to carry out both the first and the second fractionation.

By moving the packing material bed counter-currently to the liquid flow direction of the dry solids profile, an actual moving bed system can be achieved. It is self-evident that results very similar to those achieved with a simulated moving bed can be obtained with such an actual moving bed.

In the method of the invention, preferably a gel-type strong cation exchanger (e.g. "Dowex", "Finex" or "Purolite") is employed as the packing material for the columns, and it is preferably in sodium and/or potassium form. The packing material is preferably equilibrated to the ionic form of the feed solution prior to the fractionation.

The dry solids content of the beet-derived sucrose-containing solution to be fed to the chromatographic separation is typically 20-80 g/100 g, preferably 40-70 g/100 g. The solution is heated to 40-95°C, preferably 65-85°C, prior to being supplied to the separation process.

The elution phase employs mainly water and/or very dilute aqueous solutions (having a dry solids content less than 8% by weight, preferably less than 1% by weight). The eluant has a temperature of 40-95°C, preferably 65-85°C.

The dry solids content of the betaine fraction obtained from the first fractionation is adjusted prior to the second fractionation to about 25-50 g/100 g for batch separation or, typically, to 20-80 g/100 g, preferably 40-70 g/100 g, for SMB separation.

Sucrose can be recovered from the sucrose fraction by methods commonly used in the sugar industry, such as by crystallization or as a syrup, or as liquid sugar subsequent to purification. Betaine is at least partly recovered from the betaine fraction obtained from the second fractionation. This can be performed by crystallization, for example, as described in international application WO 81/02420, or said fraction can be used as a concentrated betaine solution.

To optimize the sucrose and betaine yields and purity, the pH of the feed solution may also be adjusted. It is generally adjusted prior to the second fractionation to the range 6.5-12, and preferably between 9.5 and 11.5.

The following examples illustrate the method of the invention in the context of fractionating beet molasses to recover sucrose and betaine. These examples are not to be construed as limiting the scope of the invention, but they are only illustrative of the special embodiments of the invention.

Example 1

Sequential SMB method; separation of sucrose and betaine from molasses without further separation of betaine fraction (reference example)

A chromatographic apparatus as schematically shown in Figure 1 was employed. The apparatus comprised three columns 1-3 connected in series, fluid conduits 4-7 connecting the columns, a molasses container 8, a water/eluant container 9, a molasses feed conduit 10, an eluant feed conduit 11, a recycle pump 12, a molasses feed pump 13, an eluant feed pump 14, heat exchangers 15-17, product fraction withdrawal conduits 6, 18-20, 48 and 49, and valves 21-47. The apparatus further comprised flow and pressure regulators (not shown).

The columns were packed with a strong cation ex-

changer resin Finex CS 11 GC™, manufacturer Finex Oy. The resin had a polystyrene/divinylbenzene backbone and was activated with sulphonic acid groups; the mean bead size (in Na^+ form) was about 0.38 mm. The resin had a DVB content of 5.5%. Prior to the test, the resin was regenerated to sodium form; during the fractionation it was equilibrated by cations from the feed solution.

Test conditions:

Diameter of columns	0.2 m
Total height of resin bed	10.5 m
Temperature	80°C

The feed solution was beet molasses wherefrom calcium was precipitated by adding sodium carbonate (pH about 9); the calcium carbonate precipitate was removed by filtration.

Fractionation was performed by a seven-step sequence that comprised the following steps:

Step 1: Feed solution 10 was introduced (feeding phase) into column 1 at a flow rate of 80 l/h, and a residue fraction was eluted from the downstream end of the same column 2 through conduit 48. Simultaneously, eluant was supplied (eluting phase) to column 2 through valve 26 at a flow rate of 25 l/h, and a sucrose fraction was eluted from column 3 through conduit 6.

Step 2: The liquid in the columns was recycled (recycling phase) in the loop formed by all columns at a rate of 120 l/h.

Step 3: Eluant was introduced into column 1 through valve 23 at a rate of 120 l/h and, simultaneously, a betaine fraction was eluted from column 3 through conduit 6.

Step 4: Eluant 11 was introduced (eluting phase) into column 1 through valve 23 at a flow rate of 120

l/h, and a second residue fraction was eluted from the downstream end of column 2 through conduit 49. Simultaneously, eluant was supplied (eluting phase) to column 3 through valve 29 at a flow rate of 55 l/h, and a second betaine fraction was eluted from the downstream end of the same column through conduit 6.

Step 5: Same as step 2.

Step 6: Eluant 11 was introduced into column 1 through valve 23 at a flow rate of 120 l/h, and a third residue fraction was eluted from the downstream end of column 3 through conduit 6.

Step 7: Same as step 2.

After the sequence was carried to completion, the process control program was continued and it returned to step 1. By repeating this sequence five to seven times, the system was equilibrated. The method proceeded in a state of equilibrium, and the progress of the separation process was monitored with a density meter, a meter for optical activity, and a conductivity meter, and the separation was controlled by a microprocessor whereby precisely defined volumes and flow rates of feeds, recycled liquid and product fractions were controlled employing quantity/volume measuring means, valves and pumps.

In this method, a sucrose fraction from column 3, two betaine fractions from column 3, and one residue fraction from each column were withdrawn. The betaine fractions were combined, as were the residue fractions.

Analyses of the feed solution and the product fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 1, where the percentages of the different components are given as per cent by weight dry solids basis.

Table 1

	Dry solids g/100 g	Sucrose %	Betaine %
Feed solution	46.5	58.1	5.2
Sucrose fraction	25.8	92.1	0.8
Betaine fraction (combined)	4.2	18.1	55.6
Residue fraction (combined)	5.0	12.7	4.5

The sucrose yield into the sucrose fraction was 90.1% and the betaine yield into the combined betaine fraction 58.7%.

Example 2

Sequential SMB method; separation of sucrose and betaine from molasses, further separation of betaine fraction

The apparatus and test conditions described in Example 1 were employed. The procedure was also similar to that of Example 1, except that a higher purity, but lower yield, for sucrose and a lower purity, but higher yield, for betaine than in Example 1 were obtained in the first fractionation by adjusting the fraction volumes. Subsequent to evaporation, the resulting betaine fraction was subjected to re-fractionation by a similar sequential SMB method. The sucrose fraction obtained from the second fractionation was combined with the sucrose fraction from the first fractionation, and the residue fractions were likewise combined.

Analyses of the feed solutions and the product fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 2, where the percentages of the different components are given as per cent by weight dry solids basis.

Table 2

	Dry solids g/100g	Sucrose %	Betaine %
First fractionation			
Feed solution	46.5	58.1	5.2
Sucrose fraction	25.5	92.6	0.4
Betaine fraction	3.3	21.3	43.9
Residue fraction	4.8	11.7	0.9
Second fractionation			
Feed solution	55.0	21.3	43.9
Sucrose fraction	14.0	82.6	1.0
Betaine fraction	8.3	1.1	85.2
Residue fraction	4.1	11.2	2.2
Combined product fractions			
Sucrose fraction	24.7	92.2	0.4
Residue fraction	4.7	11.7	1.0

The sucrose yield from the first fractionation was 89.4% and the betaine yield was 89.9%. The total sucrose yield, calculated from the combined sucrose fraction, was 92.6% and the total betaine yield, calculated from the betaine fraction obtained from the second fractionation, was 88.2%. The second fractionation afforded remarkable improvement of the sucrose yield and betaine purity. In addition, the betaine yield improved significantly as compared with Example 1.

Example 3

The method described in Example 2 was essentially followed, but the effect of the pH of the feed solution for the second fractionation (which solution had been obtained from the betaine fraction from the first fractionation) was studied, performing the second fractionation in such a way that (a) the pH of the feed solution was not adjusted, and, hence, the pH was 10.2, (b) the

pH of the feed solution was adjusted with hydrochloric acid to 9.5, and (c) the pH of the feed solution was adjusted with NaOH to 11.2.

Analyses of the feed solution for the second fractionation (i.e. further separation of the betaine fraction) and the product fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 3, where the percentages of the different components are given as per cent by weight dry solids basis.

Table 3

	Dry solids g/100 g	Sucrose %	Betaine %
Feed solution	43.0	32.5	24.8
(a) pH 10.2			
Sucrose fraction	16.6	84.6	0.1
Betaine fraction	6.2	0.4	89.3
(b) pH 9.5			
Sucrose fraction	17.9	81.1	0.1
Betaine fraction	6.2	0.4	88.0
(c) pH 11.2			
Sucrose fraction	15.4	82.5	0.1
Betaine fraction	6.1	0.1	90.4

The yields from the second fractionation in the above cases (a), (b) and (c) were as follows:

(a) sucrose 57.3%, betaine 95.4%

(b) sucrose 59.6%, betaine 96.8%

(c) sucrose 51.9%, betaine 96.8%.

As will be seen from the results, the pH of the feed solution affects the purity and yield of sucrose and betaine. The pH may be adjusted in accordance with the economical optimum.

Example 4

Continuous SMB method; separation of sucrose and by-product fraction from molasses (reference example)

The test apparatus comprised 14 columns connected in series, each having a diameter of 0.2 m and each containing a packing material bed having a height of 0.85 m. Figure 2 shows a schematic diagram of the test apparatus.

The columns were packed with a polystyrene-based cross-linked (5.5% DVB) strong cation exchanger having a mean bead size of 0.32 mm. The packing material was equilibrated with feed solution and was predominantly in potassium and sodium form.

Water, as eluant, was introduced into the column system at a flow rate of 83.5 l/h. Feed solution was introduced through conduit 51 at each feed point at a flow rate of 13.5 l/h for 150 seconds. The feed conduits were rinsed with eluant (30 s, 13.5 l/h) subsequent to the introduction of the feed solution. The flow rate of the product fraction through valves 66-79 was adjusted to 21 l/h, which produced a by-product flow rate of 76 l/h. The by-product fraction was withdrawn through a spring-biased valve securing the desired pressure for the system. An average recycle rate of 300 l/h was maintained. In practice, this rate varies according to the change of the relative positions of the feed introduction and product withdrawal points along the recirculation loop. The points of introduction of the feed solution and eluant and the withdrawal points of the product fractions were shifted downstream one column each successive step at intervals of 180 seconds.

Initially, the system was filled with a higher feed flow rate and lower eluant flow rate. Once the system was filled, the flow rate setpoints stated above were used to run the system until an equilibrium had

been established.

Samples were taken at two-minute intervals via a sampling valve placed in the recirculation loop. The concentration gradient shown in Figure 3 was drawn on the basis of an analysis of the samples. In addition, the feed solution and the product and by-product fractions were analysed. The results are shown in Table 4, where the percentages of the different components are given as per cent by weight on a dry solids basis.

Table 4

	Feed solution	Product fraction	By-product fraction
Dry solids content, g/100 g	65.0	25.3	4.9
Sucrose, %	60.4	87.2	19.0
Betaine, %	5.5	4.5	7.0
Raffinose, %	2.1	0.9	4.0
Others, %	32.0	7.4	70.0
Flow rate, l/h	13.5	21.0	76.0
Sucrose yield into sucrose fraction 87.6			

Example 5

Continuous SMB method for separation of sucrose and betaine from molasses and batch method for further separation of betaine fraction

Molasses was fractionated by the continuous SMB method, wherein the column system of Example 4 was modified in such a way that it was possible to withdraw three product fractions: sucrose, betaine, and by-product fractions. Figure 4 shows a schematic diagram of the test apparatus. The flow rate of the sucrose fraction was adjusted to 21 l/h and the flow rate of the betaine fraction to 18 l/h. The feed rate of the eluant through

conduit 94 was 90.5 l/h, and the feed flow rate through conduit 95 was 13.5 l/h. Hence, the flow rate of the by-product fraction through conduit 96 was 65 l/h.

The betaine fraction was concentrated to a dry solids content of 55% and fed to a separation system comprising two columns connected in series. The columns had a diameter of 0.2 m, and the packing material bed in each column had a height of 0.85 m. The packing material was the same as in Example 4.

The betaine fraction was further fractionated using the batch method, supplying 2.6 l of feed solution (55% by weight on a dry solids basis) to the upstream end of the first column. The feed was repeatedly introduced at intervals of 60 minutes. Elution was performed at a flow rate of 30 l/h. The following fractions were withdrawn from the bottom of the column:

Fraction 1: By-product 8.6 l
Fraction 2: Recycle fraction 2 l (introduced into the column prior to the actual feed)
Fraction 3: Product solution 2.6 l
Fraction 4: Recycle fraction 1.4 l (introduced into the column subsequent to the actual feed)
Fraction 5: Betaine fraction 5.0 l
Fraction 6: Elution recycling 10 l

With this procedure and column distribution, the betaine separation has a capacity more than twice the capacity of a single column system comprising 14 columns with respect to the betaine fraction produced.

The filling and equilibration of the column system, sampling, and analyses of the samples were performed as above. The concentration gradient from the first continuous SMB separation is shown in Figure 5. The results are shown in Table 5, where the percentages of the different components are given as per cent by weight on a dry solids basis.

Table 5

Fractionation of molasses, continuous SMB						
	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %	Flow rate l/h
Feed solution	65.0	60.4	5.5	2.1	32.0	13.5
Sucrose fraction I	25.2	87.6	4.5	0.9	7.0	21.0
Betaine fraction I	3.5	45.2	31.1	0.4	23.3	18.0
By-product fraction I	4.9	13.7	2.3	4.6	79.4	65.0
Sucrose yield into sucrose fraction 87.6% Betaine yield into betaine fraction 37.0%						
Fractionation of betaine fraction, batch method						
Feed solution	55.0	45.2	31.1	0.4	23.3	
Sucrose fraction II	22.8	92.6	2.2	0.2	5.0	
Betaine fraction II	10.3	5.4	88.3	0.0	6.3	
By-product fraction II	4.5	18.0	3.2	1.2	77.6	
Sucrose yield into sucrose fraction 86.2% Betaine yield into betaine fraction 94.5%						
Combined sucrose and by-product fractions						
Sucrose fraction I + II	25.1	87.8	4.4	0.9	6.9	
Betaine fraction II	10.3	5.4	88.3	0.0	6.3	
By-product fraction I + II	4.8	13.9	2.3	4.5	79.3	
Sucrose yield into sucrose fraction 91.8% Betaine yield into betaine fraction 35.0%						

As can be seen from the results, the yield of sucrose increased from 87.6% to 91.8% and the purity of sucrose increased from 87.2% to 87.8%. With this simple modification, betaine was recovered with a yield of about 35% and a purity of 88.3%. The low betaine yield is a result of the continuous SMB method in which the feed flow was uninterrupted, and thus a considerable portion of the betaine was lost in the sucrose fraction. By increasing the eluant flow rate and increasing the flow rate of the betaine fraction proportionately, the betaine yield may increase up to about 50-60%.

Example 6

Sequential SMB method for separation of sucrose and betaine from molasses and further separation of betaine fraction

The continuous SMB method disclosed in Example 4 was converted into a sequential method in such a way that the columns of Example 4, referred to as sectional packing material beds herein, were interconnected in sequence to form a four-column system in which two columns were formed by sectional packing material beds 1-3 and 4-6, and two columns by sectional packing material beds 7-10 and 11-14. Thus, the system comprised two columns having a total sectional packing material bed height of 2.55 m each, and two columns having a total sectional packing material bed height of 3.4 m each. Figure 6 shows a schematic diagram of the apparatus.

Fractionation was performed sequentially by the following eight-step sequence:

Step 1: 15 l of feed solution was introduced into sectional packing material bed 1 at a flow rate of 75 l/h, and a by-product fraction was withdrawn from sectional packing material bed 10. 20 l of eluant was introduced into sectional packing material bed 11 at a flow rate of 100 l/h, and a sucrose fraction was withdrawn

from sectional packing material bed 14.

Step 2: 8 l of liquid was recycled at a flow rate of 100 l/h in the loop formed by all columns.

Step 3: 12 l of eluant was introduced into sectional packing material bed 1 at a flow rate of 120 l/h and a by-product fraction was withdrawn from sectional packing material bed 3. Simultaneously, 12 l of eluant was supplied to sectional packing material bed 4 at a flow rate of 120 l/h, and a betaine fraction was withdrawn from sectional packing material bed 14.

Step 4: 14 l of eluant was introduced into sectional packing material bed 1 at a flow rate of 120 l/h, and a betaine fraction was withdrawn from sectional packing material bed 14.

Step 5: 8 l of liquid was recycled at a flow rate of 100 l/h in the loop formed by all columns.

Step 6: 10 l of eluant was introduced into sectional packing material bed 1 at a flow rate of 100 l/h, and a by-product fraction was withdrawn from sectional packing material bed 14.

Step 7: 4 l of eluant was introduced into sectional packing material bed 1 at a flow rate of 120 l/h, and a by-product fraction was withdrawn from sectional packing material bed 14.

Step 8: 12 l of eluant was introduced into sectional packing material bed 7. The profile was shifted by way of recirculation to sectional packing material bed 1, and a by-product fraction was withdrawn from sectional packing material bed 6.

The betaine fraction was concentrated to a dry solids content of 55% and introduced into a separation system comprising three columns. Figure 7 shows a schematic diagram of the apparatus. The columns had a diameter of 0.2 m, and the packing material bed in each column had a height of 0.85 m. The packing material was

the same as in Example 4.

Fractionation was performed sequentially by the following eight-step sequence:

Step 1: 2 l of feed solution was introduced into column 1 at a flow rate of 60 l/h, and a by-product fraction was withdrawn from column 2. 2.7 l of eluant was supplied to column 3 at a flow rate of 80 l/h, and a sucrose fraction was withdrawn from column 3.

Step 2: 1.5 l of feed solution was supplied to column 1 at a flow rate of 60 l/h, and a sucrose fraction was withdrawn from column 3.

Step 3: 1.5 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

Step 4: 3 l of eluant was introduced into column 1 at a flow rate of 60 l/h, and a betaine fraction was withdrawn from column 3.

Step 5: 1.8 l of eluant was introduced into column 1 at a flow rate of 54 l/h, and a by-product fraction was withdrawn from column 1. Simultaneously, 4 l of eluant was supplied to column 2 at a flow rate of 120 l/h, and a betaine fraction was withdrawn from column 3.

Step 6: 3 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

Step 7: 1.5 l of eluant was introduced into column 1 at a flow rate of 60 l/h, and a by-product fraction was withdrawn from column 3.

Step 8: 3 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

With this procedure, the betaine separation has more than double the capacity of the first separation stage with respect to the amount of the betaine fraction produced. Thus, it was not attempted in this test to optimize the sequence with respect to capacity and energy consumption, but good yields and purities were pursued. This resulted in low fraction concentrations.

It is obvious to those skilled in the art that, in actual industrial practice, optimization is realized on an economic basis, thus the optimum values may be rather different from the values disclosed herein.

The filling and equilibration of the column system, sampling, and analyses of the samples were performed similarly as in Example 4. The concentration gradient from the output of sectional packing material bed 14 in the first continuous SMB separation is shown in Figure 8. The results are shown in Table 6, where the percentages of the different components are given as per cent by weight on a dry solids basis.

Table 6

	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %
Fractionation of molasses, sequential SMB					
Feed solution	55.0	60.4	5.5	2.1	32.0
Sucrose fraction I	24.3	92.3	0.9	1.2	5.6
Betaine fraction I	3.9	44.9	45.5	0.7	8.9
By-product fraction I	5.9	14.1	0.6	4.0	81.3
Sucrose yield into sucrose fraction 84.1%					
Betaine yield into betaine fraction 87.3%					
Fractionation of betaine fraction, sequential SMB					
Feed solution	55.0	44.9	45.5	0.7	8.9
Sucrose fraction II	22.5	91.7	5.3	0.5	2.5
Betaine fraction II	16.0	7.4	88.9	0.0	3.7
By-product fraction II	3.0	25.3	1.0	5.5	68.2
Sucrose yield into sucrose fraction 87.0%					
Betaine yield into betaine fraction 94.8%					
Combined sucrose and by-product fractions					
Sucrose fraction I + II	24.2	92.3	1.2	1.1	5.4
Betaine fraction II	16.0	7.4	88.9	0.0	3.7
By-product fraction I + II	5.7	14.4	0.6	4.0	81.0
Sucrose yield into sucrose fraction 91.0%					
Betaine yield into betaine fraction 82.8%					

As can be seen from Figure 8, significantly better separation of betaine from sucrose is achieved compared to the fully continuous method of Example 5. Table 6 shows that with substantially similar column loads, the sequential method also yields a considerably higher purity of 92.3%, for the sucrose fraction than the 87.2-87.8% for the fully continuous method. Double separation permits the first fractionation to be performed with a relatively low sucrose yield, e.g. 84.1%, thus realizing the need for a high separation capacity and low evaporation. Double separation increases the sucrose yield to 91.0%. The betaine yield may easily be increased to 82.8%, and with a higher eluant quantity and column capacity, the betaine yield may exceed 90%.

Example 7

Continuous SMB method for the separation of by-product and a combined sucrose and betaine fraction from molasses followed by a continuous SMB method for the separation of sucrose fraction and betaine fraction from the combined sucrose and betaine fraction

The test apparatus and resin described in Example 4 were used for the experiment.

Water, as eluant, was introduced into the column system at a flow rate of 144.6 l/h. Feed solution was introduced through conduit 51 at each point at a flow rate of 23 l/h for 165 seconds. The feed conduits were rinsed with eluant (15 s, 22.9 l/h) subsequent to the introduction of the feed solution. The flow rate of the product fraction through valves 66-79 was adjusted to 33.9 l/h, which produced a by-product flow of 133.7 l/h. The by-product was withdrawn through a spring-biased valve securing the desired pressure for the system. An average recycle rate of 290 l/h was maintained. In practice, this rate varies according to the change of the relative positions of the feed introduction and product

withdrawal points along the recirculation loop. The points of introduction of the feed solution and eluant and the withdrawal points of the product fractions were shifted downstream one column each successive step at intervals of 180 seconds.

As stated in Example 4, the system was allowed to reach an equilibrium before sampling.

When the recycling rate is lowered in relation to the feed and product flow rates, more betaine will end up in the product fraction than in Example 4. The sucrose purity of the product fraction will be lower (85.6% instead of 87.2%). However, the separation capacity will be significantly higher.

The product fraction from this separation, containing most of the sucrose and betaine, was collected and used as a feed solution in a similar continuous SMB system. No evaporation was needed, the product fraction was used as such.

Water, as eluant, was introduced into the column system at a flow rate of 42.4 l/h. Feed solution was introduced through conduit 51 at each point at a flow rate of 34.9 l/h for 300 seconds. The feed conduits were rinsed with eluant (10 s, 34.9 l/h) subsequent to the introduction of the feed solution. The flow rate of the betaine fraction through valves 66-79 was adjusted to 37.9 l/h, which produced a sucrose fraction flow of 39.4 l/h. The by-product was withdrawn through a spring-biased valve securing the desired pressure for the system. An average recycle rate of 170 l/h was maintained. In practice, this rate varies according to the change of the relative positions of the feed introduction and product withdrawal points along the recirculation loop. The points of introduction of the feed solution and eluant and the withdrawal points of the product fractions were shifted downstream one column each successive step

at intervals of 310 seconds.

The results of this test are shown in Table 7. It is to be seen that the results are clearly better than when it is attempted to obtain three product fractions from a continuous SMB system, as set forth in Example 5. The final betaine purity is lower (52.5% instead of 88.3%), but the overall recovery of betaine is much better (63.7% instead of 35%) and, more importantly, the purity of the sucrose fraction is significantly higher (93.6% instead of 87.8%). The final sugar product can be recovered by crystallization of this sucrose fraction and, owing to the high purity, the yield from the crystallization will be significantly higher. It is also possible to purify this high-quality sucrose fraction by ion exchange and adsorption techniques into a colourless or nearly colourless liquid sugar product or syrup.

Table 7

Fractionation of molasses, continuous SMB						
	Dry solids content (DS) g/100 g	Sucrose % of DS	Betaine % of DS	Raffinose % of DS	Others % of DS	Flow rate l/h
Feed solution	65.0	60.4	5.5	2.1	32.0	23.0
Product fraction	30.7	85.6	6.0	0.8	7.5	33.9
By-product fraction	4.7	13.8	4.6	4.4	77.2	133.7
Sucrose yield into product fraction			92.0%			
Betaine recovery into product fraction			70.8%			
Fractionation of product fraction, continuous SMB						
Product fraction	30.7	85.6	6.0	0.8	7.5	34.9
Sucrose fraction	24.1	93.6	0.7	0.8	5.0	39.9
Betaine fraction	3.2	16.6	52.5	1.6	29.2	37.4
Sucrose yield into sucrose fraction			98.0%			
Betaine yield into betaine fraction			90.0%			
Overall sucrose yield into sucrose fraction			90.2%			
Overall betaine yield into betaine fraction			63.7%			

Claims:

1. A method for separating sucrose and additionally a second dissolved component from a beet-derived sucrose-containing solution, characterized in that the solution is subjected to a first fractionation by a chromatographic simulated moving bed method to yield a sucrose-enriched fraction and a fraction enriched with the second dissolved component or a fraction enriched with sucrose and the second dissolved component, and the resulting fraction enriched with the second component or with sucrose and the second dissolved component is subjected to a second chromatographic fractionation, to yield a second sucrose-enriched fraction and a separate fraction enriched with the second dissolved component.

2. A method as claimed in claim 1, characterized in that a fraction enriched with sucrose and, separately therefrom, a fraction enriched with the second dissolved component are recovered in the first fractionation.

3. A method as claimed in claim 2, characterized in that the second sucrose-enriched fraction is combined with the sucrose fraction from the first chromatographic fractionation, and sucrose is recovered from the combined sucrose fraction thus obtained.

4. A method as claimed in claim 2, characterized in that the second sucrose-enriched fraction is returned to the feed solution for the first chromatographic fractionation, and sucrose is recovered from the sucrose-enriched fraction obtained from the first fractionation.

5. A method as claimed in claim 1, characterized in that a fraction enriched with sucrose

and the second dissolved component are recovered in the first fractionation.

6. A method as claimed in claim 5, c h a r a c t e r i z e d in that sucrose is recovered from the second sucrose-enriched fraction.

7. A method as claimed in any one of claims 1-6, c h a r a c t e r i z e d in that the second dissolved component is recovered at least partly from the fraction enriched with said second dissolved component and obtained from the second fractionation.

8. A method as claimed in any one of claims 1-7, c h a r a c t e r i z e d in that the second dissolved component is selected from betaine, inositol, raffinose, galactinol, and serine and other amino acids.

9. A method as claimed in claim 8, c h a r a c t e r i z e d in that the second dissolved component is betaine.

10. A method as claimed in any one of claims 1-9, c h a r a c t e r i z e d in that the simulated moving bed method is a continuous simulated moving bed method.

11. A method as claimed in any one of claims 1-9, c h a r a c t e r i z e d in that the simulated moving bed method is a sequential simulated moving bed method.

12. A method as claimed in any one of claims 1-11, c h a r a c t e r i z e d in that the second fractionation is performed by a batch method.

13. A method as claimed in any one of claims 1-11, c h a r a c t e r i z e d in that the second fractionation is performed by a continuous simulated moving bed method.

14. A method as claimed in any one of claims 1-11, c h a r a c t e r i z e d in that the second fractionation is performed by a sequential simulated moving bed method.

15. A method as claimed in any one of claims 1-

14, c h a r a c t e r i z e d in that the beet-derived sucrose-containing solution is beet molasses.

16. A method as claimed in any one of claims 1-15, c h a r a c t e r i z e d in that the chromatographic fractionation is performed with a strong cation exchanger.

17. A method as claimed in claim 15, c h a r a c t e r i z e d in that the cation exchanger is a polystyrene-based cation exchanger cross-linked with divinylbenzene and having a divinylbenzene content of 4-8%.

18. A method as claimed in claim 16 or 17, c h a r a c t e r i z e d in that the cation exchanger is predominantly in sodium and/or potassium form.

19. A method as claimed in any one of claims 1-18, c h a r a c t e r i z e d in that the dry solids content of the solution fed to the second fractionation is adjusted.

20. A method as claimed in any one of claims 1-19, c h a r a c t e r i z e d in that the pH of the solution fed to the second fractionation is adjusted to the range 6.5-12.

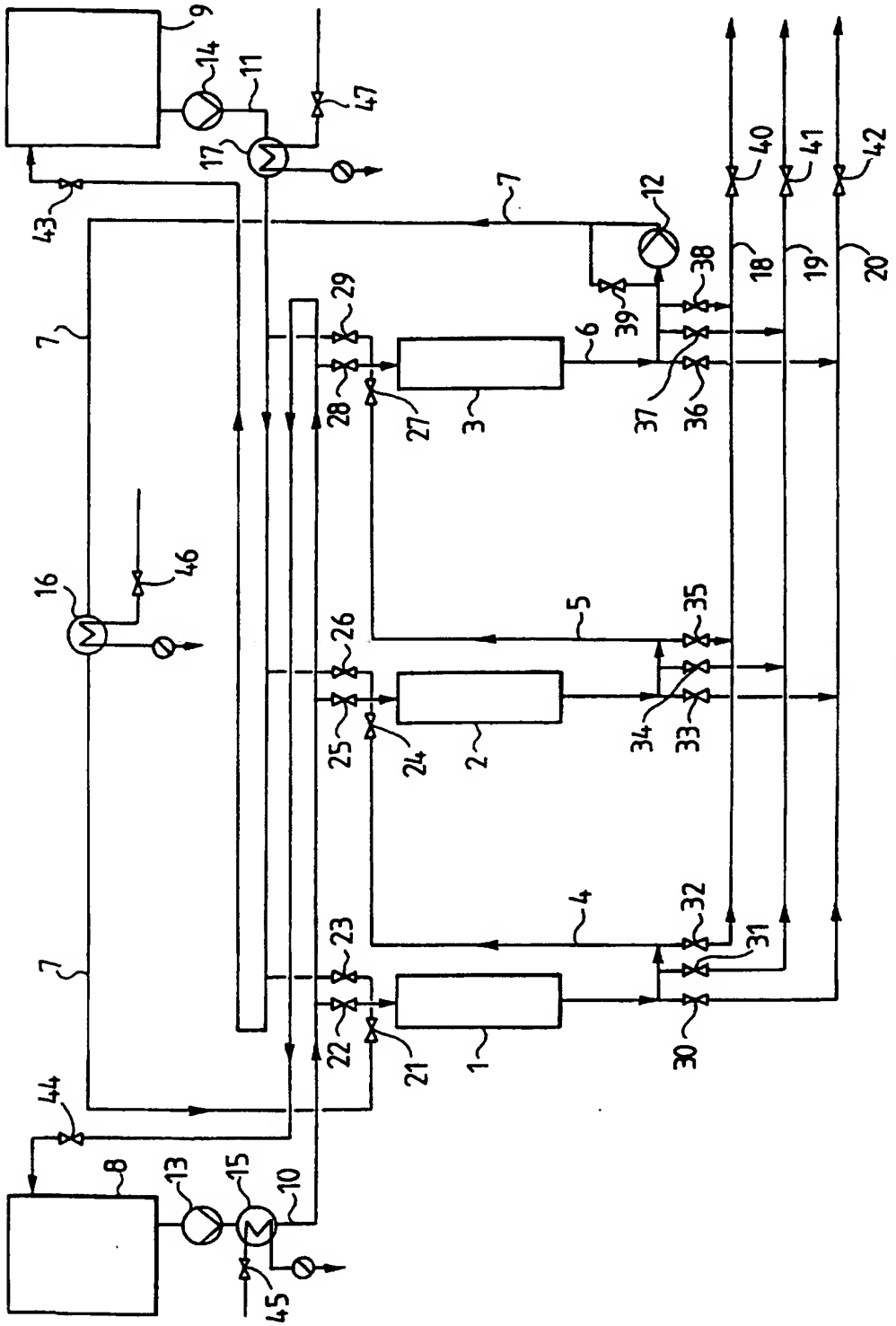
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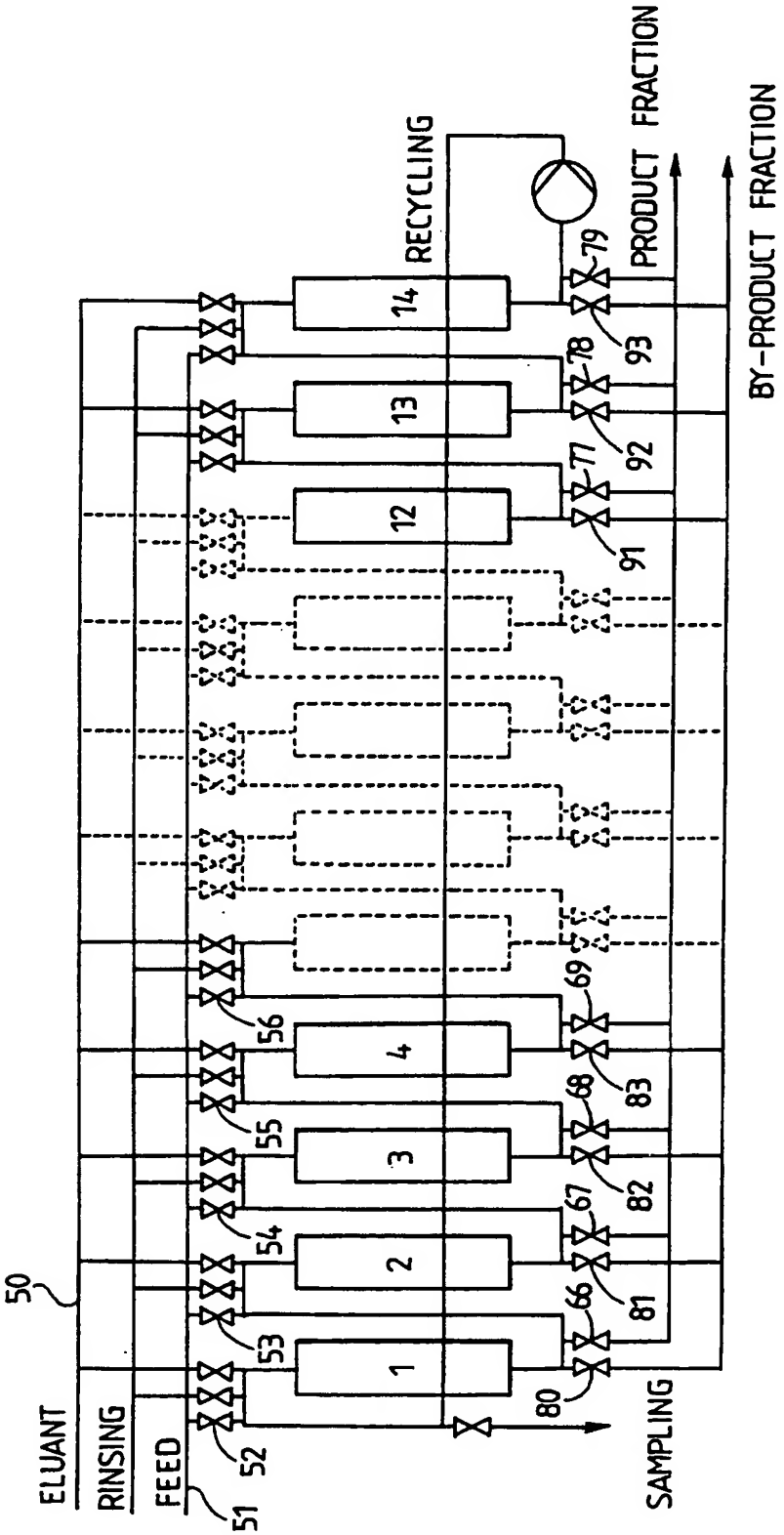
FIG. 1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BY-PRODUCT FRACTION
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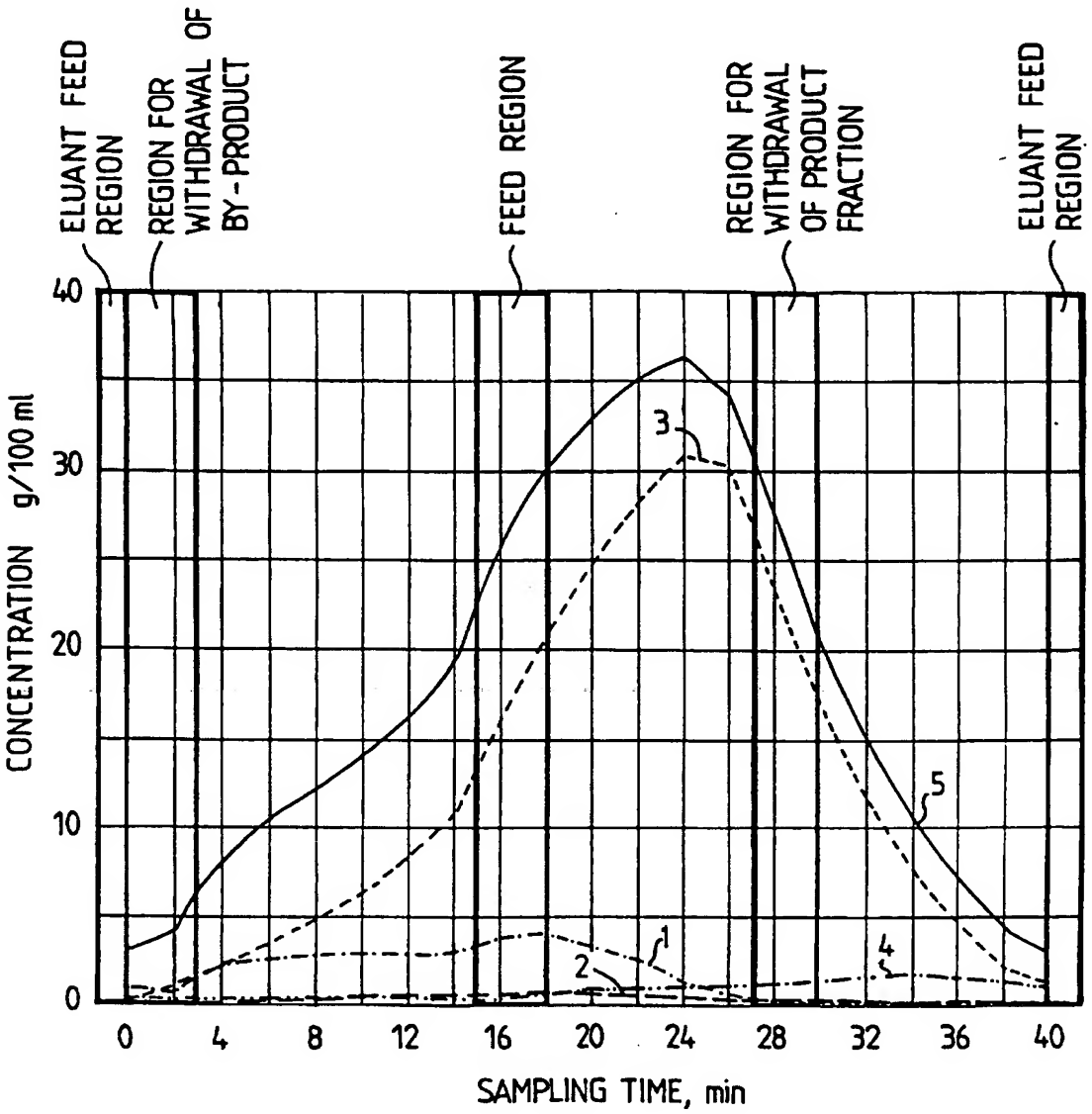
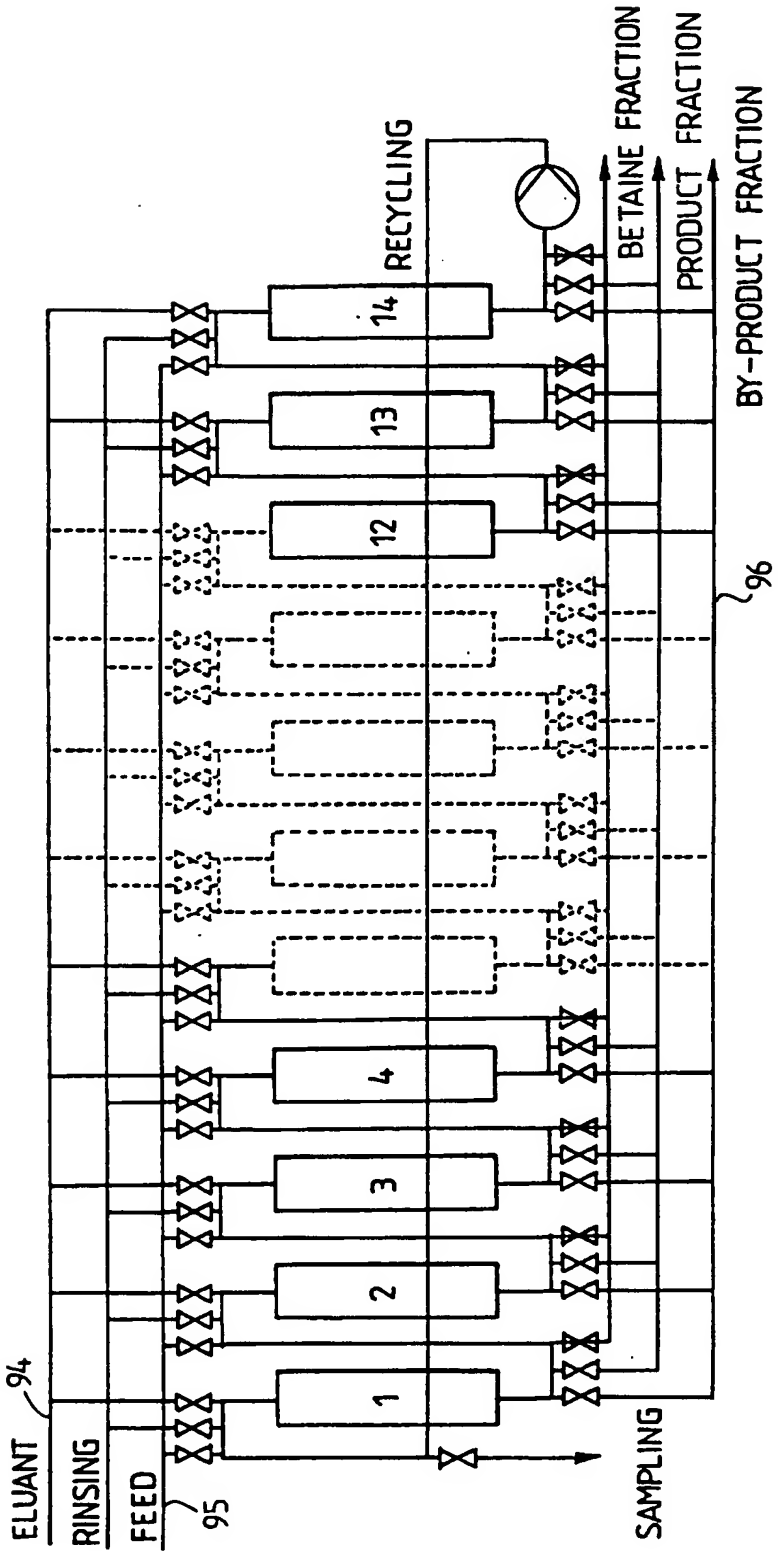
SAMPLING

FIG. 2



1 SALTS (HPLC)
2 RAFFINOSE
3 SUCROSE
4 BETAINE
5 CONCENTRATION

FIG. 3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PRODUCT FRACTION
BY-PRODUCT FRACTION
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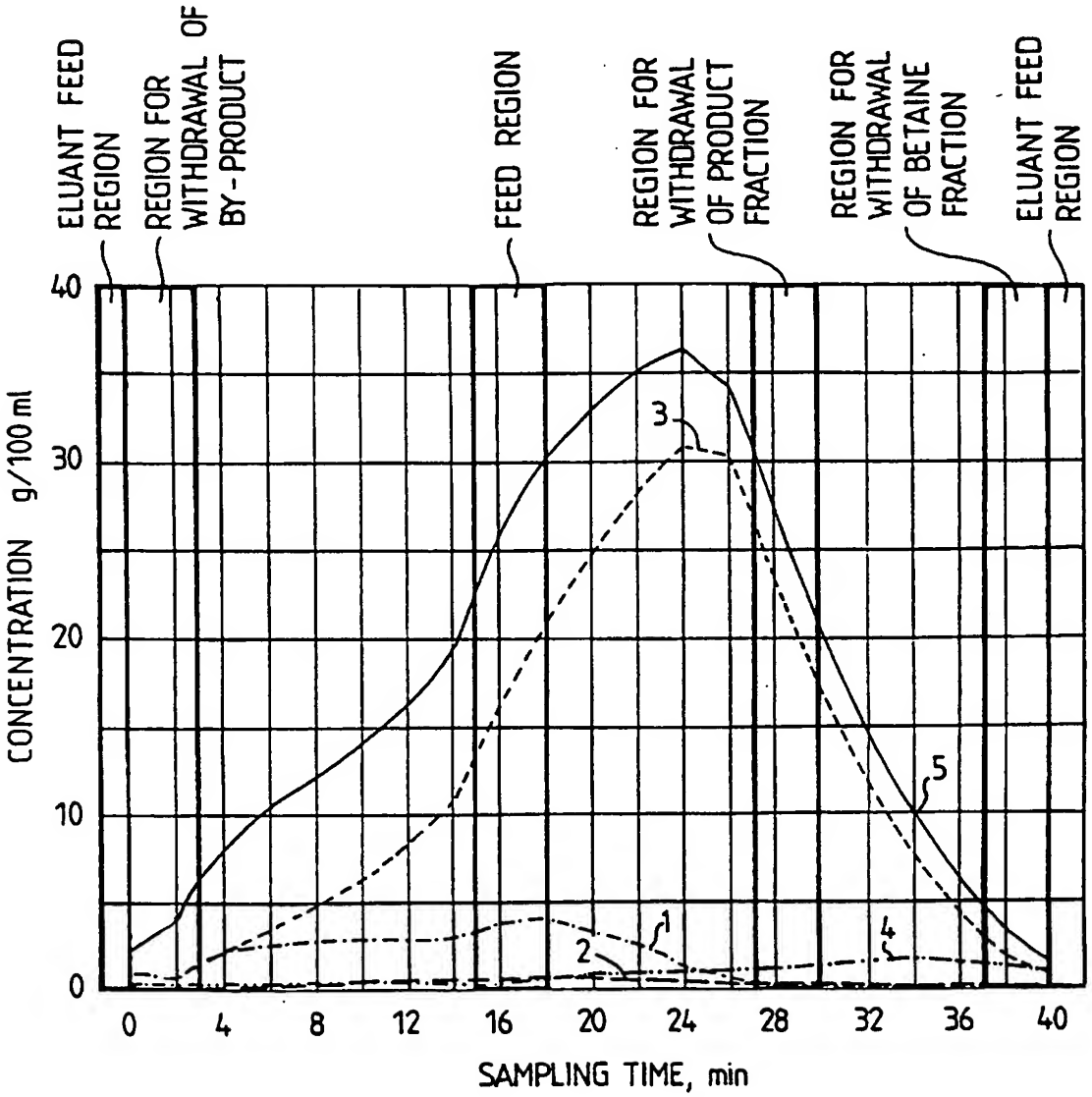
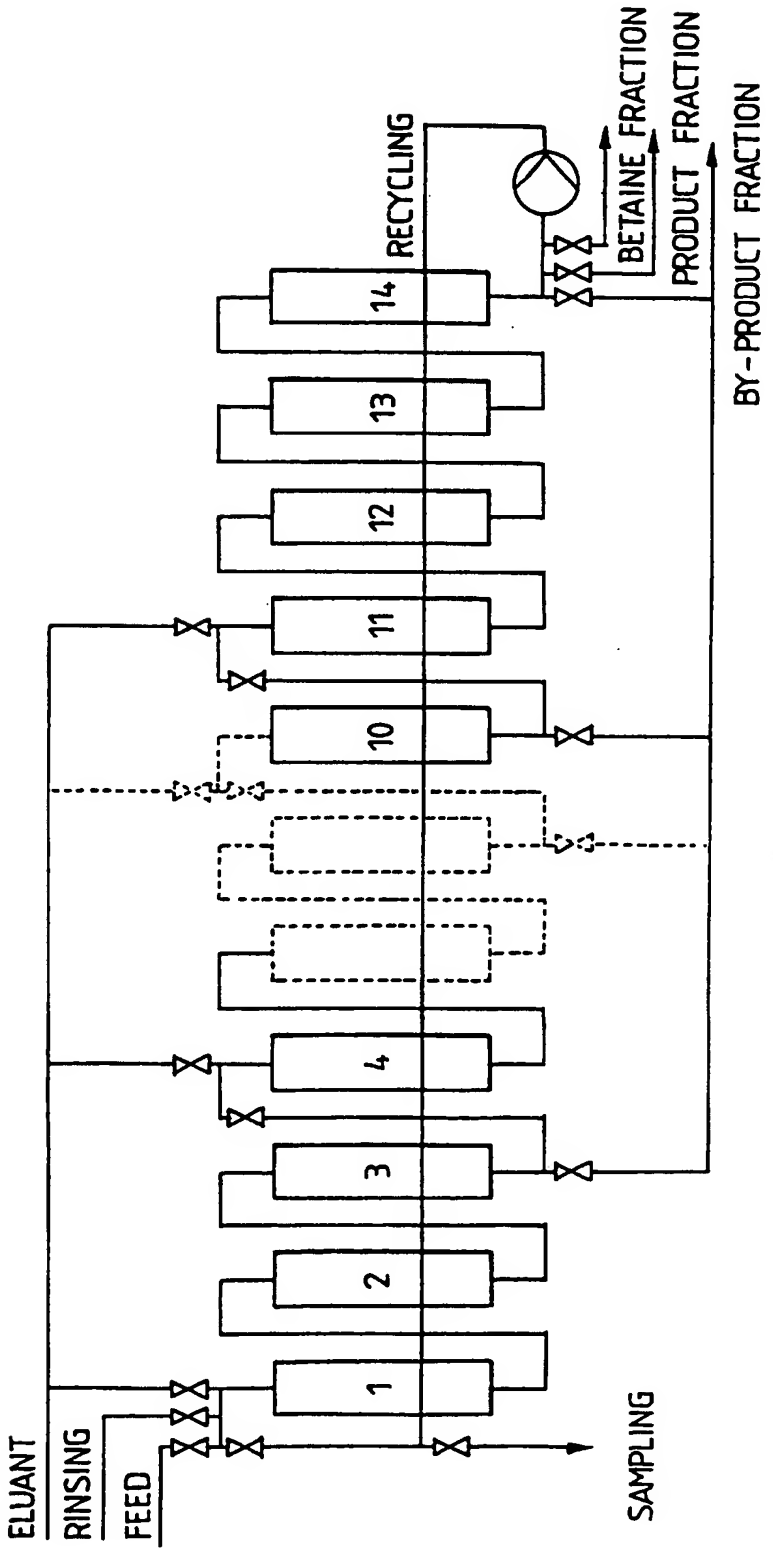
FIG. 4



1 SALTS (HPLC)
2 RAFFINOSE
3 SUCROSE
4 BETAINE
5 CONCENTRATION

FIG. 5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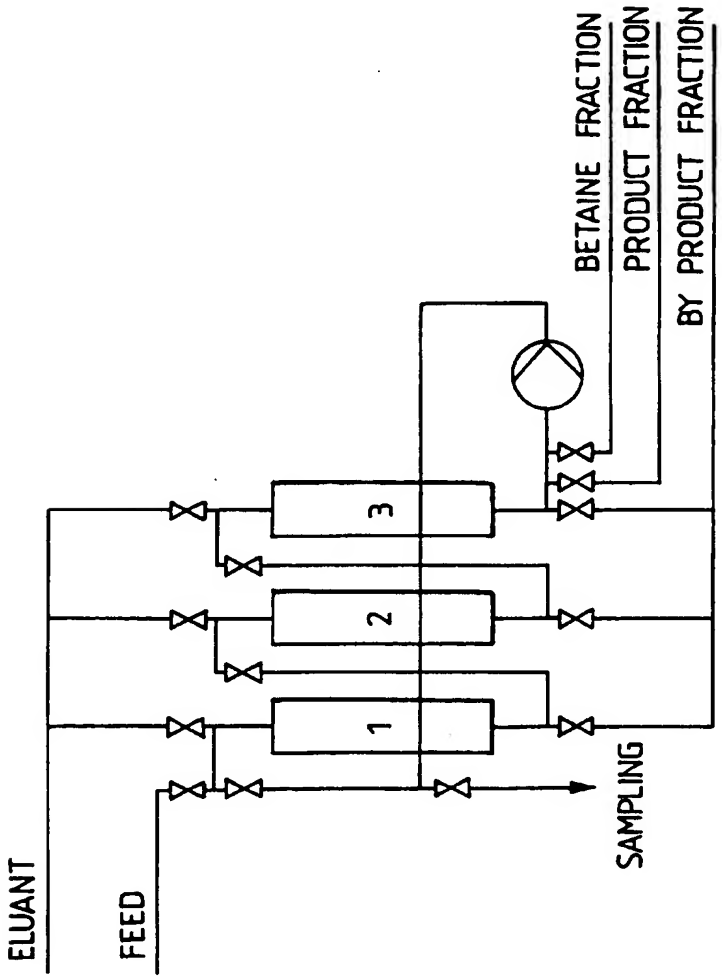
BETAINE FRACTION
PRODUCT FRACTION
BY-PRODUCT FRACTION

FIG. 6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PRODUCT FRACTION
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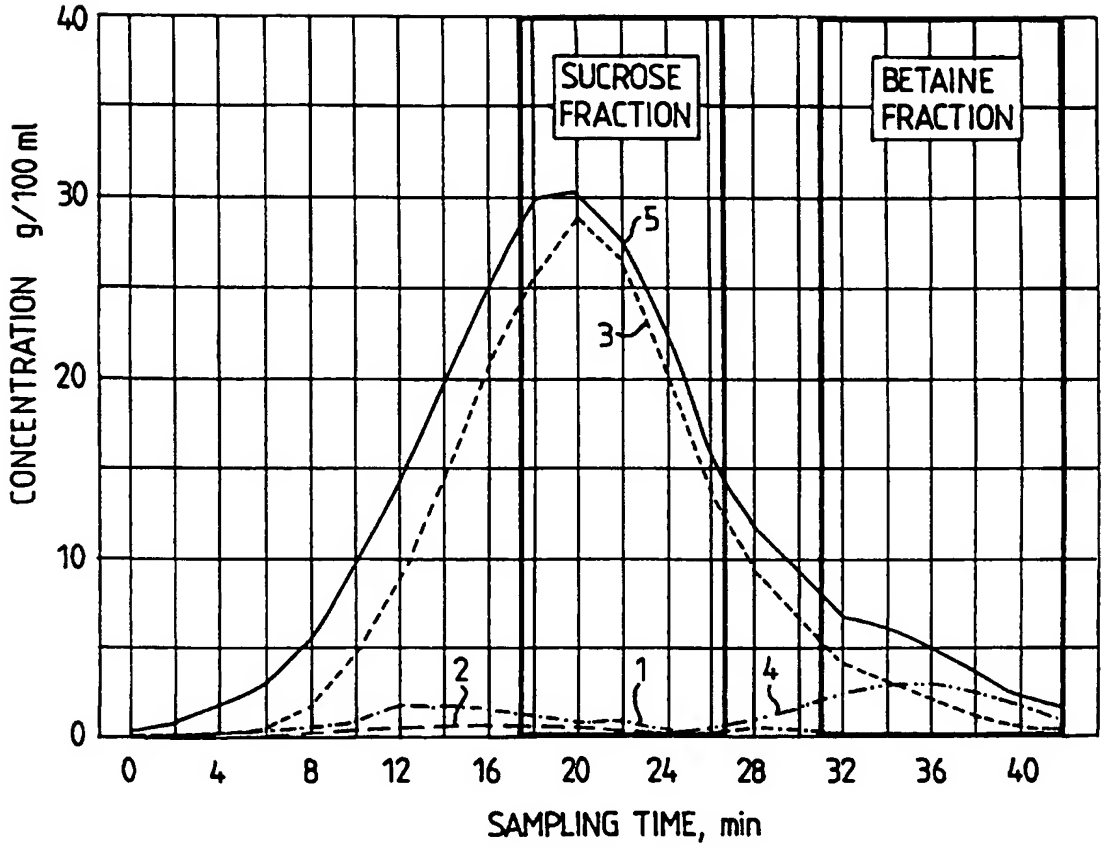
SAMPLING
ELUANT
FEED

FIG. 7



1 SALTS (HPLC)
2 RAFFINOSE
3 SUCROSE
4 BETAINE
5 CONCENTRATION

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00538

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C13D 3/14, C13J 1/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C13D, C13J, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, IFIPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9417213 A1 (H. HEIKKILÄ ET AL), 4 August 1994 (04.08.94) --	1-20
Y	US 5217957 A (H. HEIKKILÄ ET AL), 7 July 1992 (07.07.92) --	1-20
A	WO 8102420 A1 (H. HEIKKILÄ ET AL), 3 Sept 1981 (03.09.81) --	1-20
A	EP 0101304 A2 (C.G. GERHOLD), 22 February 1984 (22.02.84) --	1-20

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 January 1996	12 -02- 1996
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Gerd Strandell Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00538

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2985589 A (D.B. BROUGHTON ET AL), 23 May 1961 (23.05.61) --	1-20
A	US 5102553 A (M.M. KEARNEY ET AL), 7 April 1992 (07.04.92) --	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

05/01/96

International application No.
PCT/FI 95/00538

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9417213	04/08/94	NONE	
US-A- 5217957	07/07/92	AU-A- 2543992	16/03/93
		WO-A- 9303721	04/03/93
		ZA-A- 9206245	21/02/94
WO-A1- 8102420	03/09/81	AT-E,T- 11132	15/01/85
		BE-A,A- 887652	15/06/81
		EP-A,B- 0054544	30/06/82
		SE-T3- 0054544	
		US-A- 4359430	16/11/82
EP-A2- 0101304	22/02/84	SE-T3- 0101304	
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		AU-A- 1763383	16/02/84
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		JP-T- 4502276	23/04/92
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